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MANUFACTURE OF AROMATIC CARBONIC ACID ESTERS

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### Abstract

#### Objective

To offer a simple catalyst system that is used in the manufacture of aromatic carbonic acid esters via a reaction between an aromatic hydroxy compound, carbon monoxide and oxygen, where compounds that contain metal ions having a redox action and auxiliary catalysts or complex bases are not used.

#### Constitution

A catalyst system is used that comprises (A) one or more substances selected from palladium and palladium compounds, (B) one or more inorganic halides selected from alkali metal halides and alkaline earth metal halides, and (C) activated carbon.

### Claims

1. A method for manufacturing aromatic carbonic acid esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing aromatic carbonic acid esters being characterized in that said reaction is carried out in a reaction system in the presence of (A) one or more substances selected from palladium and palladium

compounds, (B) one or more inorganic halides selected from alkali metal halides and alkaline earth metal halides, and (C) activated carbon.

2. The method according to Claim 1, wherein the aforementioned palladium compound is an organic acid salt of palladium.

3. The method according to Claim 1, wherein the aforementioned inorganic halide is a chloride or bromide.

4. The method according to Claim 1, wherein the aforementioned inorganic halide is cesium chloride or cesium bromide.

#### Detailed explanation of the invention

[0001]

#### Industrial application field

The present invention concerns a method for the manufacture of aromatic carbonic acid esters using a special catalyst. Aromatic carbonic acid esters, particularly diphenyl carbonate, are useful as raw materials in the production of polycarbonate and other substances.

[0002]

#### Prior art

In the past, methods wherein an aromatic hydroxy compound and phosgene are allowed to react have been used as methods for

manufacturing aromatic carbonic acid esters. However, these methods are undesirable due to the high toxicity of phosgene. Thus, a number of methods have been offered that do not use phosgene whereby aromatic carbonic acid esters are manufactured in a reaction between an aromatic hydroxy compound, carbon monoxide and oxygen.

[0003]

With regard to catalysts that are used in such methods, a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38144 wherein a palladium compound, a compound containing a metal from group IIIA, IVA, VA, VIA, IB, IIB, VIB or VIIB of the periodic table and a base are used; a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38145 wherein a palladium compound, manganese complex, cobalt complex, base and desiccant are used; a method is described in Japanese Kokai Patent Application No. Hei 1[1989]-165551 wherein a palladium compound, iodine compound and zeolites are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-104564 wherein a palladium compound, divalent or trivalent manganese compound, tetraalkylammonium halide and quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-142754 wherein a palladium compound, divalent or trivalent cobalt compound, tetraalkylammonium halide and quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-25095 wherein a palladium compound, cobalt compound, organic or inorganic halide and basic compound are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-58961 wherein a palladium compound,

cobalt compound, and alkali metal halide are used; and a method is offered in Japanese Kokai Patent Application No. Hei 5[1993]-97775 wherein a palladium compound, inorganic auxiliary catalyst selected from cobalt, iron, cerium, manganese, molybdenum, samarium, vanadium, chromium and copper, an organic auxiliary catalyst selected from an aromatic ketone, aliphatic ketone or aromatic polycyclic hydrocarbon, and a quaternary ammonium salt are used.

[0004]

Means to solve the problems

Conventional catalyst systems used in the manufacture of aromatic carbonic acid esters have had complicated reaction systems that require the use of costly complex salts to increase yields, that require the use of an auxiliary catalyst such as a quaternary ammonium salt, and that also require the use of redox agents containing manganese, copper, cobalt, cerium and other metal ions. In addition, separation and purification of the aromatic carbonate ester that is produced is difficult. Moreover, the yields of aromatic carbonic acid esters in conventional methods have not been very high, and it has been necessary to recover the catalyst component in order to make the process more practical. Quaternary ammonium salts are particularly unstable under reaction conditions, and because phenol bromide, for example, is generated in large amounts, the process for recovering said component is extremely difficult for conventional complicated catalyst systems. The objective of the present invention is thus to offer a method for manufacturing the target

aromatic carbonic acid esters at high yields using a catalytic system that is simpler than those used in the past.

[0005]

Means to solve the problems

The inventors of the present invention et al. thus carried out painstaking investigations towards the development of a method for manufacturing aromatic carbonic acid esters at high yields and with high selectivity using a simple catalytic system that does not include complex bases and auxiliary catalysts of compounds that contain metal ions having a redox function. As a result, the present invention was realized when it was discovered that the aforementioned objectives can be achieved using a special catalyst system. Specifically, the present invention is a method for manufacturing aromatic carbonic acid esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing aromatic carbonic acid esters being characterized in that said reaction is carried out in a reaction system in the presence of (A) one or more substances selected from palladium and palladium compounds, (B) one or more inorganic halides selected from alkali metal halides and alkaline earth metal halides, and (C) activated carbon.

[0006]

## Specific description of the invention

### 1. Reaction raw materials

#### (1) Aromatic hydroxy compound

The aromatic hydroxy compound that is used in the present invention is an aromatic mono- or polyhydroxy compound. Examples include phenol; cresol, xylenol, trimethylphenol, tetramethylphenol, ethylphenol, propylphenol methoxyphenol, ethoxyphenol, chlorophenol, dichlorophenol, bromophenol, dibromophenol and other substituted phenols and isomers thereof; naphthol, methylnaphthol, ethylnaphthol, chloronaphthol, bromonaphthol and other substituted naphthols and isomers thereof; 2,2-bis(4-hydroxyphenyl)propane and various other bisphenols; various biphenols; various hetero-aromatic hydroxy compounds and isomers thereof; as well as compounds thereof produced by substitution with alkyl groups or halogen atoms. Of these compounds, phenol is particularly desirable.

[0007]

#### (2) Carbon monoxide

The carbon monoxide that is used in the present invention can be a gas that is produced by starting with a high-purity substance and diluting it with another gas that does not have a



detrimental influence on the reaction, such as nitrogen, argon, carbon dioxide or hydrogen.

[0008]

### (3) Oxygen

The oxygen that is used in the present invention can be a gas that is produced by starting with a high-purity substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as air, nitrogen, argon, carbon dioxide or hydrogen.

[0009]

## 2. Catalyst

The catalyst that is used in the reaction of the present invention comprises the three components (A)-(C) below.

### (A) Palladium or palladium compounds

The palladium and palladium compounds that are used in the present invention are palladium black; palladium/carbon, palladium/alumina, palladium/silica or other substances carrying palladium; palladium chloride, palladium bromide, palladium iodide, palladium sulfate, palladium nitrate or other inorganic palladium salts; and palladium acetate, palladium oxalate, palladium formate, palladium benzoate or other organic palladium acid salts. In addition, substances that can also be used include

palladium (II) acetylacetonate, palladium complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins with palladium, examples of which include  $\text{PdCl}_2(\text{PhCN})_2$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ ,  $(\text{Pd}(\text{NH}_3)_4)\text{Cl}_2$ , and  $\text{Pd}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ , or mixtures of palladium with compounds generated by these complexes in the reaction system. Of these substances, organic acid palladium salts are preferred, with palladium acetate being particularly desirable. The amount of palladium component that is used in the reaction is in the range of  $10^{-6}$  to 1 in terms of mole ratio with respect to the aromatic hydroxy compound, with a range of  $10^{-5}$  to  $10^{-1}$  being particularly desirable.

[0010]

(B) Inorganic halide

The halide that is used in the present invention is an alkali metal or alkaline earth metal halide. Examples of preferable halides include chlorides and bromides, such as lithium chloride, cesium chloride, sodium bromide, potassium bromide, rubidium bromide, cesium bromide and barium bromide. Of these substances, cesium chloride and cesium bromide are particularly desirable. There are no particular restrictions on the amount of inorganic halide that is used in the present invention, but a mole ratio in the range of  $10^{-2}$  to  $10^3$  with respect to the palladium component (A) is preferred, with a range of  $10^{-1}$  to  $10^2$  being particularly desirable.

[0011]

(C) Activated carbon

The activated carbon that is used in the present invention can be a commercially available substance, and the raw materials that can be used include wood, coconut husk, coal and pitch systems. There are no particular restrictions on the amount of activated carbon that is used in the reaction, but 20-200x by weight with respect to the palladium metal is used, with a range of 50-150x being particularly desirable.

[0012]

3. Reaction conditions

The reaction is performed by introducing the aforementioned aromatic hydroxy compound and catalyst comprising the aforementioned components (A), (B) and (C) into the reactor, pressurizing the system with carbon monoxide and oxygen, and carrying out the reaction while heating. The reaction pressure is  $10^{-2}$  to 50 MPa, with  $10^{-1}$  to 25 MPa being preferred. From the standpoint of safety, it is preferable for the compositional ratio of carbon monoxide and oxygen to be outside the combustion range. The reaction temperature is in the range of 20-300°C, with 60-250°C being preferred, and 80-130°C being additionally desirable. The reaction time is a few minutes to few hours. It is also effective to add desiccant such as a molecular sieve to the reaction system, or to carry out the reaction while removing water that is generated from the reaction system. Examples of

solvents that can be used in the reaction include hexane, heptane, cyclohexane, benzene, toluene, xylene, methylene chloride, chloroform, chlorobenzene, diethyl ether, diphenyl ether, tetrahydrofuran, dioxane, ethyl acetate, methyl formate, acetonitrile and other inert solvents. There are cases where the raw material aromatic hydroxy compound serves as the reaction solvent, and it is not particularly necessary to use another solvent in such cases.

[0013]

#### Application examples

The present invention is described in detail below by providing application examples and comparative examples.

##### Application Example 1

3.0 g (32 mmol) of phenol, 2.7 mg (0.012 mmol Pd) of palladium acetate, 40 mg (0.238 mmol) of cesium chloride and 100 mg of activated carbon (C/Pd = 77 weight ratio) (Maruko P, "manufactured by Nimura Kagaku Kogyo) were introduced into a Hastelloy autoclave with a volume of 30 mL. The interior of the system was replaced with carbon monoxide, and carbon monoxide was introduced at 6 MPa, while dry air was introduced at 3 MPa. The reaction was carried out for 3 h at 100°C, and the reaction solution was then analyzed by gas chromatography. Diphenyl carbonate was obtained at a yield of 4.87% (0.78 mmol). In addition, phenyl salicylate was obtained as by-product at 0.09% (0.014 mmol), and p-phenoxyphenol was produced at 0.37%

(0.059 mmol).

[0014]

#### Application Example 2

A reaction was allowed to occur in the same manner as in Application Example 1, with the exception that the reaction time was changed to 5 h. The diphenyl carbonate yield was 5.84% (0.93 mmol).

[0015]

#### Application Example 3

A reaction was allowed to occur in the same manner as in Application Example 1, with the exception that the used amount of activated carbon was changed to 120 mg (C/Pd = 92 weight ratio). Diphenyl carbonate was obtained at a yield of 5.27% (0.84 mmol).

[0016]

#### Comparative Example 1

3.0 g (32 mmol) of phenol, 2.7 mg (0.012 mmol Pd) of palladium acetate, 4.1 mg (0.012 mmol) of cerium (III) acetate monohydrate, and 40 mg (0.238 mmol) of cesium chloride were introduced into a Hastelloy autoclave with a volume of 30 mL. After replacing the interior of the system with carbon monoxide, carbon monoxide was introduced at 6 MPa, while dry air was